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(71) Applicant: **THE GLIDDEN COMPANY**  
925 Euclid Avenue  
Cleveland Ohio 44115 (US)

(72) Inventor: **Craun, Gary Pierce**  
409 Crescent Drive  
Berea, Ohio 44017 (US)  
Inventor: **Rosekelly, George Stephne**  
15209 Athens Avenue  
Lakewood, Ohio 44107 (US)  
Inventor: **Floyd, Frederick Louis**  
1400 East-West Highway,  
Apartment 523  
Silver Springs, Maryland 20910 (US)

(74) Representative: **Cooper, Alan Victor et al**  
ICI Group Patents Services Dept.  
PO Box 6  
Shire Park  
Bessemer Road  
Welwyn Garden City Herts, AL7 1HD (GB)

(54) **Latex paints with microemulsion modifier and process for their preparation.**

(57) An aqueous ambient dry paint coating based on an addition copolymer matrix polymer containing an oligomer selected from a polyurethane or a polyester having a T<sub>g</sub> below -20°C and a number average molecular weight between 200 and 20,000, where the coating is free of organic coalescing solvents. The matrix polymer comprises emulsion copolymerized ethylenic monomers. In a preferred process, the oligomer is produced by forming an aqueous micro-preemulsion of oligomer in water by high shear mixing of oligomer and water containing 40% to 70% by weight oligomer and at temperatures between about 20°C and 100°C to provide an aqueous pre-emulsion having an organic phase droplet size less than 10 microns. The polymeric binder can be produced also by mixing the oligomer with the ethylenic monomers to form an organic mixture of monomer and oligomer, providing an aqueous micro dispersion of the organic mixture phase droplet size less than 5 microns, and copolymerizing the monomer to produce a vinyl acetate polymer containing oligomer. The polymeric binder system is free of coalescing organic solvent.

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This invention pertains to air dry emulsion paints based on emulsion polymeric binders and more particularly to odour-free, consumer latex paints free of polluting offensive odouriferous coalescing solvents.

## BACKGROUND OF THE INVENTION

Paint coatings are surface protective coatings applied to substrates, dried to form continuous films for decorative purposes as well as to protect the substrate. Consumer paint coatings are air-drying aqueous coatings applied primarily to architectural interior or exterior surfaces, where the coatings are sufficiently fluid to flow out, form a continuous paint film, and dry at ambient temperatures to protect the substrate surface. A paint coating ordinarily comprises an organic polymeric binder, pigments, and various paint additives. In dried paint films, the polymeric binder functions as a binder for the pigments and provides adhesion of the dried paint film to the substrate. The pigments may be organic or inorganic and functionally contribute to opacity and color in addition to durability and hardness, although some paint coatings contain little or no opacifying pigments and are described as clear coatings. The manufacture of paint coatings involves the preparation of a polymeric binder, mixing of component materials, grinding of pigments in a dispersant medium, and thinning to commercial standards.

Latex paints for the consumer market ordinarily are based on polymeric binders prepared by emulsion polymerization of ethylenic monomers. A typical consumer latex paint binder contains a vinyl acetate copolymer consisting of polymerized vinyl acetate (80%) and butyl acrylate (20%). The hardness of the latex polymer must be balanced to permit drying and film formation at low application temperatures, which requires soft polymer units, while at the same time the polymer must be hard enough in the final film to provide resistance properties which requires hard polymer units. This is conventionally accomplished by designing a latex polymer with a moderately elevated T<sub>g</sub> (glass transition temperature) but then lowering the T<sub>g</sub> temporarily with a volatile coalescing solvent. Coalescing solvents function to externally and temporarily plasticize the latex polymer for time sufficient to develop film formation, but then diffuse out of the coalesced film after film formation, which permits film formation and subsequent development of the desired film hardness by the volatilization of the coalescent. Internal plasticization is based on coreaction of soft monomers with hard monomers to form a polymeric copolymer binder, such as 80/20 vinyl acetate/butyl acrylate, to obtain the desired film forming characteristics. If a lower T<sub>g</sub> copolymer is used without a coalescing solvent, higher levels of soft comonomer are required leading to lower T<sub>g</sub> polymer, and, hence, the final dried film would be undesirably soft, excessively tacky, readily stain, and readily pick up dirt.

A significant source of residual odour in latex consumer paints is directly due to the coalescing solvent. Coalescing solvents are typically linear (or slightly branched) glycol ethers and esters of 7 to 12 carbon atoms in length, which have boiling points typically above 200°C, and solubility parameters appropriate for the latex of interest. One typical coalescing solvent ordinarily contained in commercial latex paints is 2,2,4-trimethylpentanediol monoisobutyrate (Texanol® Eastman Chemical Co.). The odour associated with the gradual volatilization of this solvent is considered objectionable by consumers. Quite often the odour lingers for days or weeks after the paint is applied and dried. All useful coalescing solvents are volatile and have similar objectionable characteristics. An additional deficiency in conventional exterior latex paints is the decline in crack resistance of the dried paint film approximately proportional to the evaporation of the coalescing solvent. While better coalescing solvents have a retention time of about one year in dried paint films, cracking starts to progressively appear after one year in dried paint films. Hence, any elimination of coalescing solvents and attendant objectionable odours, along with air pollution caused by volatile organic compounds (VOC), and film cracking deficiencies would represent both a technical and marketing advance in the state of the art of consumer latex paints.

In polymer technologies unrelated to air-dry vinyl acetate latex paints, preformed polymers have been dispersed into monomers and emulsified in water, whereupon the monomers are then polymerized, such as disclosed in U.S. 4,373,054 pertaining to cathodic electrocoating, or in U.S. 4,313,073 pertaining to alkyd prepolymers; U.S. 4,588,757 pertaining to laminating adhesives, or in U.S. 3,953,386 and U.S. 4,011,388 pertaining to aqueous emulsion blends containing cellulosic ester/acrylic polymers.

It now has been found that certain non-volatile softening oligomeric modifiers compatible with an aqueous emulsion addition copolymer binder in a consumer latex paint can be retained in the dried paint film permanently. Accordingly this invention provides an aqueous air-dry coating composition including an emulsion polymerised polymeric binder having a T<sub>g</sub> below 20°C which binder contains an addition copolymer of aqueous polymerised ethylenic monomers wherein the binder also contains 3 to 70% of a polyurethane and/or a polyester softening oligomer modifier having a molecular weight between 200 and 20,000 and a T<sub>g</sub> below -20°C and wherein the oligomer modifier is present in the aqueous composition in a

micro-emulsion of droplets having a droplet size of less than 10 microns. Softening oligomer modifiers of this invention can be incorporated into the paint where the oligomer will be retained permanently in the final paint film. Hence, the paint will not generate an odour while drying nor emit a residual odour from the dried paint film or otherwise emit VOC's. The softening oligomeric modifiers of this invention externally modify the emulsion copolymer matrix polymer and are not coreacted with the emulsion copolymer polymeric binder. The softening oligomeric modifiers appear to function by a chain-spacing mechanism to soften the matrix copolymers whereby the oligomeric modifiers provide low temperature film formation and tack-free films less prone to soiling at a given hardness and/or flexibility than ordinarily possible. Particularly preferred emulsion copolymer matrix polymers comprising polyvinyl acetate copolymers. A further advantage of this invention enables the use of essentially all hard polymer units of polyvinyl acetate without the need for internal plasticization (coreaction) with soft butyl acrylate polymeric units.

The present invention is based on a softening oligomeric modifiers having a low and narrow molecular weight range where the oligomer will not subsequently diffuse out of the matrix polymer when properly dispersed into the polymeric binder phase. Preferred oligomers are non-volatile oligomers having a molecular weight between about 300 and 10,000. Lower molecular weight compounds tend to be volatile and cause excessive plasticizer migration while higher molecular weight polymers lose low temperature film-forming and softening effects, although molecular weights above 10,000 and in some instances up to 20,000 can be used with softer matrix polymers.

According to a preferred process of this invention, a low molecular weight oligomer can be surprisingly dispersed by high shear into water under heat and pressure to provide a submicron emulsified aqueous mixture of oligomer stably dispersed in water. The micro-emulsified mixture in turn, can be readily mixed with various emulsion latex polymers to provide a stable mixture of dissimilar emulsions. It was found that micro-emulsions of oligomer in water having an average droplet size less than about one micron enable the oligomer particle to migrate out of the oligomer droplets then through the aqueous phase and into surrounding latex polymer particles if the oligomer is sufficiently low molecular weight oligomer. The lowest molecular weight oligomer particles move faster due to micro small size and have a small but finite solubility in water. A medium range molecular weight fraction of the low molecular weight oligomers move through the water phase into the latex particles at a slower rate extending over several hours or even a few days. The higher molecular weight fraction of the low molecular weight oligomer have essentially zero solubility in water and invariably remain within the oligomer emulsion droplets until a paint film dries, at which time these oligomer particles physically contact the latex particles and eventually migrate into the latex polymer particles during drying.

According to a desirable process of this invention, a compatible organic solution of oligomeric modifier in ethylenic monomer can be subjected to high energy shear to prepare a sub-micron size organic phase dispersed into water. Subsequent polymerization of the micronized monomer droplets produces a softened modified latex very different from conventional emulsion or suspension polymerization polymers. The micro aqueous suspension polymerization is generally necessary with the oligomeric modifiers to accomplish the required sub-micron aqueous emulsification of the monomer containing the dissolved oligomeric modifier, since the oligomer will not readily diffuse during polymerization from particle to particle across the aqueous phase.

The principal advantage of this invention is the elimination of the odour and VOC associated with volatile coalescent solvents which are intentionally volatile and intended to migrate out of the dried paint film. An additional advantage pertains to dried paint films exhibiting superior toughness obtained through the use of a hard polyvinyl acetate matrix polymer balanced with the oligomeric modifier to accommodate softening through the external addition of softening modifier while retaining the desired dried film hardness. A further advantage pertains to lower net cost for both interior and exterior paints since high cost soft monomers can be avoided, volatile coalescing agents can be eliminated and binder volume can be increased by using a permanent non-volatile softening oligomer instead of a volatile coalescent. The resulting dried paint films exhibit a superior balance of hardness and flexibility while maintaining long term flexibility. These and other advantages of this invention will become more apparent by referring to the detailed description and illustrative examples.

#### SUMMARY OF THE INVENTION

Briefly, the air-dry emulsion paint of this invention contains an oligomeric modified binder of polymerized ethylenic monomers to provide an aqueous emulsion addition copolymer binder externally modified with a non-reactive, low molecular weight, compatible oligomer selected from a polyester-urethane copolymer, a polyether-urethane copolymer, a polyurethane-urea copolymer, a polyesteramide, a polyester,

a chlorinated aliphatic hydrocarbon and a chlorinated fatty acid or ester, where between about 1% and desirably between 3% and 70% by weight of the binder comprises softening oligomer. Preferred emulsion addition copolymers comprise vinyl acetate copolymers.

In accordance with the preferred process of this invention, low molecular weight oligomer having a preferred number average molecular weight between about 300 and 5,000 is stably dispersed into water assisted with surfactants by heating a mixture of oligomer and water containing by weight between about 40% and 70% oligomer at temperatures preferably between about 45°C and 60°C, and then micronizing the heated oligomer water mixture under substantial shear to provide the stable microemulsion of oligomer dispersed aqueous emulsion having an average microemulsion droplet size less than about ten microns. The resulting oligomeric preformed microemulsion can be blended with a wide variety of vinyl acetate or acrylic latex polymers to provide a polymeric binder for paint coatings.

In accordance with a desirable process of this invention, the low molecular weight softening oligomer has a preferred number average molecular weight between 300 and 10,000 and is effectively dissolved in ethylenically unsaturated monomer to form a compatible organic mixture before forming the aqueous emulsion addition matrix polymer containing between 3% and 50% by weight oligomer. The organic mixture is dispersed into water by high shear, whereupon the ethylenic monomer is polymerized to produce a stabilized latex containing the low molecular weight oligomeric modifier.

#### DETAILED DESCRIPTION OF THE INVENTION

The air-dry emulsion paint of this invention comprises an emulsion polymer comprising an aqueous emulsion addition copolymer polymeric binder containing a non-volatile oligomeric modifier.

Suitable oligomeric modifiers in accordance with this invention comprise low molecular weight oligomers including urethanes consisting of polyester-urethane copolymers, polyether-urethane copolymers, polyurethane-urea copolymers; polyester polymer comprising polyester-amides and polyester polymers. The foregoing softening oligomeric modifiers function as effective external modifiers for latex emulsion paints, and particularly for the preferred polyvinylacetate binder for interior latex paints.

Useful non-volatile oligomeric modifiers have a number average molecular weight range between about 200 and 20,000, preferably between 300 and 10,000 and most preferably between 300 and 5,000. A preferred characterization of the oligomer modifier is in units of degree of polymerization (DP Units) which refers to the repeating monomer units without regard to molecular weight although the molecular weight is maintained relatively low as indicated. DP units defines the approximate chain length of the oligomers without regard to side units. The oligomeric modifier of this invention should have a DP between about 2 and 100, preferably between 2 and 50 and most preferably between 2 and 20 DP units. Useful oligomer modifiers have low Tg's to sufficiently impart a plasticizing effect on the matrix emulsion copolymer. Useful Tg's of the oligomeric modifier measured by Differential Scanning Calorimetry (DSC) at 10°C/minute scan rate are less than -20°, preferably less than -40°C and most preferably below -50°C. The level of oligomer modifier needed can vary considerably in the final latex. The level required depends on the inherent softening efficiency of the oligomer (estimated by its Tg) and the Tg of the matrix (parent) polymer. The Fox equation is useful for estimating the level needed:

$$1/T_g(\text{mix}) = (W_p/T_{g,p}) + (W_m/T_{g,m})$$

where

- T<sub>g</sub>(mix) = glass transition temperature of the modified polymer (which is a mixture);
- W<sub>p</sub>, W<sub>m</sub> = weight fraction of the parent (matrix) polymer and oligomeric modifier, respectively;
- T<sub>g,p</sub>; T<sub>g,m</sub> = glass transition temperature of the parent (matrix) polymer and the oligomeric modifier, respectively.

Thus, the level of oligomeric modifier required is directly related to the Tg of the parent matrix polymer, and inversely related to the Tg of the oligomer. Hence, the lower oligomer Tg will more efficiently soften the emulsion addition matrix polymer provided the oligomer and matrix polymer are compatible.

Compatibility of a polymeric mixture is commonly said to exist when the mixture remains substantially optically clear, which indicates the two components are mutually soluble. In this invention, compatibility is intended to mean that the oligomeric modifier is soluble in the matrix polymer in the solid state. Complete compatibility is believed to exist when these conditions are met: in the solid state the mixture has a Tg (DSC, DMA) intermediate between the Tg's of the two components; the absence of component Tg transitions; the mixture Tg is smoothly dependent on level of modifier; and the mixture Tg follows a mixing rule such as the Fox equation. Tg's of mixtures depend on the Tg's of the two components, concentrations

of the two components, and compatibility of the two components. The present invention pertains to substantially compatible components.

In accordance with this invention, low molecular weight polyurethane oligomers such as polyester-urethanes, polyether-urethanes, polyether urethane-urea copolymers, and polyester polymers including  
 5 polyester-amide copolymers can be utilized as external softening oligomers in the polyvinyl acetate binder matrix polymers. Useful polyurethane copolymers typically contain urethane groups in the polymer backbone and are produced by reacting excess equivalents of diol or polyol with lesser equivalents of di- or polyisocyanate. The polyisocyanates can be di- or triisocyanates such as for example 2,4- and 2,6- toluene diisocyanate, phenylene diisocyanate; hexamethylene or tetramethylene diisocyanate, 1,5-naphthalene  
 10 diisocyanate, ethylene or propylene diisocyanate, trimethylene or triphenyl or triphenylsulfone triisocyanate, and similar di- or triisocyanates. The polyisocyanate can be generally selected from the group of aliphatic, cyclo-aliphatic and aromatic polyisocyanates such as for example hexamethylene 1,6-diisocyanate, isophorone diisocyanate, diisocyanate, 1,4-dimethyl cyclohexane, diphenylmethane diisocyanate 2,4-toluene diisocyanate, 2,6-toluene diisocyanate and mixtures thereof, polymethylene polyphenyl polyisocyanate.

15 Polyester-urethanes can be produced from diols comprising hydroxyl functional polyester polymer prepared by conventional esterification polymerization techniques from the common dicarboxylic acids and dihydroxyl functional reactants. Suitable carboxylic acids include adipic acid, succinic acid and anhydride, azelaic acid, maleic acid and anhydride, and other aliphatic carboxylic acids. Aromatic dicarboxylic acids include isophthalic acid, phthalic acid and anhydride, terephthalic acid, trimellitic anhydride and the like.  
 20 Lesser amounts of mono-functional acids can be included, such as benzoic acid, 2-ethylhexanoic acid, if desired. Suitable dihydroxy functional materials include ethylene and propylene glycol, dipropylene glycol, diethylene glycol, neopentyl glycol, trimethylol propane, and lesser amounts of mono-functional alcohols such as benzyl alcohol and hexanol, if desired. Polyester prepolymers are generally prepared with excess hydroxyl functionality at molecular weights ranging from about 100 to 10,000 preferably about 200 to 2,000.  
 25 Polyester prepolymers can be used alone or in combination with polyethers as hydroxyl functional prepolymers. Suitable hydroxyl functional polyether prepolymers include polyethylene oxide, polypropylene oxide, polybutylene oxide, and tetramethylene oxide where the polyether prepolymers have a molecular weight between about 100 and 10,000. Preferred polyethers used in the preferred process have a number average molecular weight between about 300 and 5,000.

30 The polyesters and/or polyether prepolymers are then reacted with diisocyanate to advance the prepolymers to a molecular weight of about 200 to 20,000 and preferably between 300 and 10,000, and most preferably between 300 and 5,000, to form polyester or polyether urethane oligomers of this invention. Diisocyanates are used preferably at an equivalent ratio of about 1 isocyanate group to 1.1 to 10 hydroxyl groups. Ratios of about 1.5 to 3 hydroxyl groups per isocyanate group are preferred. Preferred  
 35 diisocyanates include toluene diisocyanate, isophorone diisocyanate, 1,6-hexane diisocyanate, diphenylmethane diisocyanate, and the like. Catalysts such as dibutyltin dilaurate, tin oxide and the like can be used to increase the isocyanate reaction rate with the hydroxyl polyester or polyether prepolymer at temperatures of about 30 to 120°C and preferably at about 70° to 100°C.

The polyester or polyether urethane copolymers can be further extended with diamine or polyamine, if  
 40 desired, to produce polyurethane-urea copolymer useful as a softening oligomer modifier in polyvinyl acetate binder matrix polymers in accordance with this invention. In this regard, primary diamine or polyamine can be added to an isocyanate terminated polyurethane intermediate containing unreacted pendant or terminal isocyanate groups obtained by reacting excess equivalents of isocyanate relative to hydroxyl equivalents in the polyester or polyether prepolymers. The primary diamines readily react with the  
 45 isocyanate functional intermediate to chain extend the polyurethane to a polyurethane-urea of a higher molecular weight. Alternatively amine can be prereacted with the diisocyanate prior to reacting with polyol. Suitable primary amines for chain extension include hexamethylene diamine, 2-methyl-pentanediamine and similar aliphatic diamines. Polyester and polyether urethane copolymers or polyurethanes extended with diamine to form polyurethane-ureas exhibit excellent compatibility with vinyl acetate monomers as well as  
 50 the resulting polyvinylacetate polymers. Polyurethane intermediate molecular weights before chain extension can be between 400 and 10,000 while after chain extension with the diamine the final molecular weight of the polyurethane-urea can be between about 800 and 20,000. Preferred polyurethanes used in the preferred process exhibit intermediate molecular weights before chain extension between 200 and 2,000 with chain extended molecular weights between 300 and 5,000.

55 A particularly preferred non-reactive oligomer useful as a softening oligomer modifier in this invention comprises a polyester polymer. In accordance with this invention, a low molecular weight ester or polyester can be dissolved in the ethylenically unsaturated monomer, suspended in water, and the aqueous suspension micronized prior to polymerization of the monomers. Useful polyester oligomers comprise

esterification reaction products of diols with dicarboxylic acids or a functional equivalent with minor amounts of polyol or polyacid if desired, to produce a low acid number polyester polymer. Suitable esters and polyesters for blending have molecular weights between about 200 and 20,000, preferably less than 10,000, and include the linear and branched esters and polyesters formed from saturated dicarboxylic acids such as adipic acid, glutaric acid, succinic acid, and other such linear aliphatic acids, acid anhydrides, and lower alkyl esters thereof; phthalic acid, isophthalic acid, trimellitic anhydride, and other aromatic acids, acid anhydrides, and lower alkyl esters thereof; monoacids such as benzoic acid, 2-ethylhexanoic acid and other aromatic and aliphatic acids, which if desired, may be used in minor amounts to end cap and limit molecular weight. Minor amounts of unsaturated dicarboxylic acids such as fumaric or maleic acid can be included, if desired, to enhance grafting with polymerized ethylenic monomers, which promotes compatibility and permanence of the oligomer in the matrix polyvinyl acetate polymer.

Diol functional materials include diethylene glycol, neopentyl glycol, 2-methyl pentane diol, ethylene glycol, butylene glycol, propylene glycol, dipropylene glycol and the like; or mono-functional glycol ether groups, such as butylcellosolve, butyl carbitol, and the like; as well as hydroxy acids such as lactic acid, and lesser amounts of triols and polyols, such as trimethylol propane and ethane, and pentaerythritol. Acids can be used in carboxyl form, anhydride form, or an ester form, such as the methyl ester form, with the above diols to form linear and branched polyesters desirably having an Acid No. below about 20, and a molecular weight between 200 and 20,000, desirably between 300 and 10,000, and preferably between about 300 and 5,000. Polyesters of diethylene or dipropylene glycol with adipic acid are preferred. The low molecular weight esters and polyesters lower the Tg of the blend and can eliminate the need for expensive comonomers such as butyl acrylate. Thus, low molecular weight esters and polyesters can be effectively used to provide excellent, non-tacky, paint films without the inclusion of coalescing solvents.

Polyester amide oligomeric modifiers are formed by the reaction of diols and diamines with dicarboxylic acids or esters. In a preferred process, methyl esters of adipic, glutaric, isophthalic or other common dicarboxylic acids are transesterified with diols and diamines at about 150°C to 250°C in the presence of common esterification catalysts such as butylstanoic acid. Typically greater amounts of diols, such as diethylene and dipropylene glycol, neopentyl glycol and the like are used with lesser amounts of diamines, such as 1,6-hexanediamine, 2-methyl pentanediamine, or the longer chain amines (e.g. Jeffamine-Texaco). Lesser amounts of monoacids, monoesters, alcohols and amines, or polyacid, polyols, or polyamines can be added, if desired.

Suitable chlorinated aliphatic modifiers useful as external plasticizers in accordance with this invention include chlorinated hydrocarbon materials selected from chlorinated paraffins, chlorinated fatty acids, and chlorinated fatty acid esters. Useful molecular weights of the chlorinated materials range from about 150 to about 5,000, and chlorine contents can range from 5% to 70% by weight. Industrially produced chlorinated materials generally are not pure compounds, but comprise a mixture of compounds with chlorine atoms substituted at various positions on the paraffin and fatty acid chain. Chlorinated paraffins for instance are chlorinated hydrocarbons having a chlorine content between about 20% and 70% by weight and preferably between 30% and 50% by weight. Chlorinated paraffins ordinarily are miscible with organic solvent including liquid ethylenic monomers, but are insoluble in water and hence will not migrate into polymer particles if added to the aqueous phase of a latex. Chlorinated fatty acids comprise chlorinated unsaturated fatty acid such as lauroleic, myristoleic, palmitoleic, oleic, recinoleic, linoleic, eleostearic, liconic, and similar fatty acid derived from linseed oil, tung oil, soybean oil, and safflower oil, and similar unsaturated vegetable oils. Chlorinated fatty acid esters are chlorinated fatty acids esterified with low molecular weight alcohols. In accordance with the process of this invention, the chlorinated compounds are soluble in the vinyl acetate monomer whereby a solution of monomer containing chlorinated paraffin or fatty acid or fatty acid esters can be suspended in water with the aid of common surfactants and very high mechanical shear or ultrasound. The chlorinated modifier can be dissolved in vinyl acetate monomer at weight levels of 1% to 90%, desirably between 3% and 50%, and preferably between 10% and 25% by weight chlorinated modifier based on the modifier and monomeric mixture.

In accordance with preferred aspects of this invention, it has been found that very low molecular weight oligomer modifier can be dispersed into water under high shear at temperatures between about 20°C and 100°C and preferably between about 45°C and 60°C, where the oligomer weight percent and the oligomer weight in the resulting emulsion is between about 40% and 70% by weight and most preferably between about 55% and 65% by weight oligomer. It has been found that high shear of the oligomer in water under these parameters produces micronized emulsion droplets having a micronized particle size below 10 microns will enable the low molecular weight oligomer to diffuse from the preformed emulsion into a preformed latex emulsion polymer. Preferred microemulsions have an average particle droplet size between 0.1 and 1 micron. The rate of diffusion increases considerably by small preemulsion particles where the rate

of diffusion is particularly fast and efficient for preformed emulsions having a particle size preferably between 0.1 and 1 micron. It has been found that efficient and complete diffusion of the low molecular weight oligomer particles can be achieved with preferred submicron emulsion particles, whereby oligomer present sufficiently diffuses into the latex particles to avoid any residual tackiness which may result from higher molecular weight residues that could not readily diffuse into the latex matrix polymer particles. Accordingly, it has been found that oligomer having a more preferred number average molecular weight below 1500 and most preferably between 500 and 1000 not only increase the quantity of oligomer diffusion, but increases diffusion efficiency into the latex matrix particles and advantageously avoids tacky film forming polymer binders. Thus, direct micronized emulsification of the oligomer into water enables the micronized preemulsion to be easily blended with a wide variety of latex emulsion matrix polymers. The resulting diffused oligomer modified latex matrix polymer comprises a plasticized latex emulsion polymer containing modifying oligomer but contains no volatile organic matter. Paint films are capable of achieving both low temperature film formation below about 10°C and tack free surfaces at ambient room temperature air dry conditions.

In accordance with this aspect of the invention, the three-dimensional solubility parameters of the oligomeric modifier must match well with that of the latex polymer in order for plasticization to occur, which may describe a boundary for this invention in term of hydrophobicity. For example, a butyl acrylate/styrene copolymer latex would require a much more hydrophobic modifier than a vinyl acetate homopolymer. In turn, the ability of the oligomeric modifier to diffuse from the microemulsion to the latex polymer should decline with decreasing hydrophobicity. This could be counteracted to some extent by reducing molecular weight although oligomeric molecular weight above about 300 are needed to maintain permanency and zero VOC conditions. Preferred oligomers are non-volatile oligomers having a molecular weight between about 300 and 5,000. Lower molecular weight compounds tend to be volatile and cause excessive plasticizer migration while higher molecular weight polymers lose low temperature film-forming and softening effects.

The oligomer preemulsion can be formed in accordance with the preferred process of the invention by forming a normally incompatible mixture of water and oligomer comprising between about 40% and 70% by weight oligomer. The oligomer can be suspended in water with mixing to form a coarse suspension using the common latex surfactants or stabilizers, such as the sulfosuccinates, the sulfates, various ethoxylated phenols, and the like. The coarse suspension is then micronized under very high shear to very fine particle size emulsion droplets of average size of less than 10 microns, preferably less than 1 micron, and most preferably less than 0.7 micron. High mechanical shear and/or ultrasound as well as other high shear devices can be used to form the microemulsion. Grinding the oligomeric modifier into an aqueous mixture of pigments is a satisfactory method of forming the micro-preemulsion. Suitable surfactants are used at about 0.1% to 5% by weight (based on solids) and include the nonionic surfactants such as various ethoxylated phenols, block copolymers of ethylene oxide and propylene oxide, anionic surfactants such as sulfosuccinates, sulfates, and sulfonates, and the like (sulfosuccinates such as hexyl, octyl, and hexadecyl sulfosuccinate are preferred). Suitable surfactants include the various sulfosuccinates such as hexyl, octyl, and hexadecyl sulfosuccinate, the various alkyl and alkyl-aromatic sulfates and sulfonates, as well as the various nonionic ethylene oxide surfactants. In accordance with this aspect of the invention, the modifying oligomers are dispersed into water and micronized into a microemulsion, whereupon the oligomer micro-preemulsion can be mixed with a preformed emulsion latex copolymer of copolymerized ethylenic monomers.

In accordance with another aspect of this invention, the oligomers can be solubilized in ethylenic monomer, then dispersed into water and micronized into a microemulsion. The ethylenic monomers are then polymerized to produce a polymeric binder comprising emulsion polymerized ethylenic monomer. The preferred ethylenic monomer is vinyl acetate, although other ethylenic monomers can be copolymerized with the vinyl acetate monomer to produce a preferred copolymer containing by weight less than 60% and preferably less than 30% and most preferably less than 20% other ethylenic monomer. The oligomers can be dissolved in the ethylenically unsaturated monomers to form a fluid organic solution containing above 1% and desirably between about 3% and 50% and preferably between 10% and 25% by weight oligomer based on the weight of the organic monomer solution. This organic mixture of oligomer and monomer is then suspended in water with high shear mixing to form a coarse suspension using the common latex surfactants as stabilizers. Suitable surfactants are used at about 0.1 to 5% by weight (based on solids) and include the nonionic surfactants such as various ethoxylated phenols, block copolymers of ethylene oxide and propylene oxide, anionic surfactants such as sulfosuccinates, sulfates, and sulfonates, and the like (sulfosuccinates such as hexyl, octyl, and hexadecyl sulfosuccinate are preferred). The coarse suspension is then micronized to very fine particle size emulsion droplets of average size of less than 5 microns, preferably less than 1 micron, and most preferably less than 0.7 micron. High mechanical shear and/or



ultrasound can be used to form the microemulsion. Typical additional ingredients include buffers, acrylic acid, sodium salt of acrylamido methyl propane sulfonic acid (NaAMPS) ordinarily added at 0.1% to 5% by weight levels based on solids. Initiators such as persulfate, peroxide, and azo initiators can be added before or after suspension of the organic mixture in water. Redox catalysts can be added if desired. Polymerization can be accomplished by simply raising the suspension temperature to about 70°C to 80°C using persulfate initiators. Initial reflux of vinyl acetate will be at 67°C, but the temperature will rise with monomer polymerization conversion. Additional ethylenic monomer can be added, preferably after the preformed suspended addition copolymer emulsion and other monomer have polymerized.

In accordance with either process of this invention, the emulsion polymerized ethylenic monomers produce a matrix polymer of polymerized monomer where the most preferred polymeric binders comprise homopolymers of vinyl acetate. On a weight basis, the polymeric binders can comprise between 40% and 100% polymerized vinyl acetate with the balance being other ethylenic monomers. Preferred polymeric binders containing at least 70% by weight polymerized vinyl acetate and most preferred 80% to 100% vinyl acetate. However, exterior latex paints based on acrylic emulsion matrix copolymers predominantly of copolymerized acrylic and styrene monomers comprising between 50% and 100% by weight acrylic monomers are particularly useful for exterior air dry latex paints. Vinyl acetate copolymers are useful for exterior paints although acrylic copolymer are preferred.

In either vinyl acetate or acrylic copolymers, other copolymerizable ethylenic monomers comprise ethylenically unsaturated monomers containing carbon-to-carbon, allylic monomers, acrylamide monomers, and mono- and dicarboxylic unsaturated acids. Vinyl esters include vinyl propionate, vinyl laurate, vinyl decanoate, vinyl butyrates, vinyl benzoates, vinyl isopropyl acetates and similar vinyl esters; vinyl aliphatic hydrocarbon monomers include vinyl chloride and vinylidene chloride as well as alpha olefins such as ethylene, propylene, isobutylene, as well as conjugated dienes such as 1,3 butadiene, methyl-2-butadiene, 1,3-pipecylene, 2,3-dimethyl butadiene, isoprene, cyclohexane, cyclopentadiene, and dicyclopentadiene; and vinyl alkyl ethers include methyl vinyl ether, isopropyl vinyl ether, n-butyl vinyl ether, and isobutyl vinyl ether. Acrylic monomers include lower alkyl esters of acrylic or methacrylic acid having an alkyl ester portion containing between 1 to 12 carbon atoms as well as aromatic derivatives of acrylic and methacrylic acid. Useful acrylic monomers include, for example, acrylic and methacrylic acid, methyl acrylate and methacrylate, ethyl acrylate and methacrylate, butyl acrylate and methacrylate, propyl acrylate and methacrylate, 2-ethyl hexyl acrylate and methacrylate, cyclohexyl acrylate and methacrylate, decyl acrylate and methacrylate, isodecyl acrylate and methacrylate, benzyl acrylate and methacrylate, and various reaction products such as butyl, phenyl, and cresyl glycidyl ethers reacted with acrylic and methacrylic acids, hydroxyl alkyl acrylates and methacrylates such as hydroxyethyl and hydroxypropyl acrylates and methacrylates, amino acrylates, methacrylates as well as acrylic acids such as acrylic and methacrylic acid, methacrylic acid, alpha-chloroacrylic acid, alpha-cyanoacrylic acid, crotonic acid, beta-acryloxy propionic acid, and beta-styryl acrylic acid. Particularly preferred comonomers include acrylates such as methyl, ethyl, propyl, butyl (linear and branched), 2-ethyl hexyl; methacrylates such as methyl, ethyl, propyl, butyl (linear and branched), 2-ethyl hexyl; vinyl esters such as acetate, propionate, butyrate, pentanoate (neo 5), nonanoate (neo 9), 2-ethyl hexanoate, decanoate (neo 10); and other ethylenic monomers such as ethylene, vinyl chloride, vinylidene chloride and butadiene. Very minor amounts of divinyl monomers such as divinyl benzene can be copolymerized if desired. For exterior latex paints, the matrix copolymer ordinarily comprises copolymerized acrylic monomers where the acrylic copolymer content can be between about 40% and 100% by weight of the copolymer.

The preferred matrix copolymer comprises emulsion polymerized vinyl acetate monomer to produce a matrix polymeric binder of polymerized vinyl acetate where the most preferred polymeric binders comprise homopolymers of vinyl acetate. On a weight basis, the preferred polymeric binders comprise between 40% and 100% polymerized vinyl acetate with the balance being other ethylenic monomers. Preferred polymeric binders contain at least 70% by weight polymerized vinyl acetate and most preferred 80% to 100% vinyl acetate. The number average molecular weight of the polymeric vinyl acetate binders should be between about 30,000 and 10,000,000 and preferably between 50,000 and 1,000,000 as measured by GPC (gel permeation chromatography) according to ASTM D3016-78, D3536-76, and D3593-80. The Tg or softening point of the modified polymeric binder particles should be less than 20°C as measured by differential scanning calorimetry, preferably less than 10°C, most preferably <5°C. The MFT (minimum film formation temperature) is an alternative measure of polymer film formation determined on the neat latex on a temperature gradient temperature bar, and is typically a few degrees higher than the Tg of the latex. MFT should be less than 20°C, preferably less than 15°C, most preferred less than 10°C. The LTFF (low temperature film formation) is a film forming test run on the fully formulated paint. LTFF typically is reported as the lowest temperature at which no cracking is observed, or alternatively, the amount of coalescent or



oligomer needed to achieve 40°F failure-free coatings. LTFF should be less than 50°F (10°C), preferably less than 40°F (5°C). The distinction with LTFF is that other paint ingredients may have either an elevating influence (fillers, pigments) or depressing (surfactants, incidental solvents in additives) effect on LTFF relative to the MFT, which is measured on the latex alone. In turn, the MFT is measured from the wet state, and therefore includes the plasticizing effect of water, while the Tg is measured on an anhydrous sample of latex film, which does not include the water plasticizing effect. Latex paints are formulated to achieve LTFF of less than 50°F (10°C), preferably less than 40°C (5°C). It is also necessary for the final dried films to not be tacky at normal use temperatures (60-110 °F). The polymeric binder contains between about 5% and 45% by weight softening oligomer with the balance being copolymer matrix polymer.

The ethylenic monomers can be polymerized in an aqueous polymerization medium by adding other emulsion polymerization ingredients. Initiators can include for example, typical free radical and redox types such as hydrogen peroxide, t-butyl hydroperoxide, di-t-butyl peroxide, benzoyl peroxide, benzoyl hydroperoxide, 2,4-dichlorobenzoyl peroxide, t-butyl peracetate, azobisisobutyronitrile, ammonium persulfate, sodium persulfate, potassium persulfate, sodium perphosphate, potassium perphosphate, isopropyl peroxydicarbonate, and redox initiators such as sodium persulfate-sodium formaldehyde sulfoxylate, cumene hydroperoxide-sodium metabisulfite, potassium persulfate-sodium bisulfite, cumene hydroperoxide-iron (II) sulfate. Redox systems consist of oxidants and reductants, which can be mixed in any pair. Transition metals such as iron can be used as accelerators for initiators for redox couples. The polymerization initiators are usually added in amounts between about 0.1 to 2 weight percent based on the monomer additions.

Suitable anionic surfactants include for example, salts of fatty acids such as sodium and potassium salts of stearic, palmitic, oleic, lauric, and tall oil acids, salts of sulfated fatty alcohols, salts of phosphoric acid esters of polyethylated long chain alcohols and phenols. Preferred anionic surfactants include for example, alkylbenzene sulfonate salts such as sodium dodecylbenzene sulfonate and salts of hexyl, octyl, and higher alkyl diesters of 2-sulfosuccinic acid. Suitable non-ionic surfactants include polyoxyethylene glycols reacted with a lyophilic compound, ethylene oxide condensation products reacted with t-octylphenol or nonylphenol and known as "Triton" surfactants, polymerized oxyethylene (IgepalCA), ethylene oxide reacted with organic acids (Emulfor), or organic acid reacted with polyoxyethylene ether of stearic or oleic acid esters (Tweens).

A paint coating composition can be produced by combining the externally modified emulsion polymer of this invention with pigments and other paint additives in a dispersing mill such as a Cowles disperser. A pigment dispersion can be preformed consisting of a dispersant and pigments on a disperser mill, a sand mill, a pebble mill, a roller mill, a ball mill or similar conventional grinding mill for milling the mineral pigments into the dispersion medium. The premix can then be combined under low shear with the polymeric binder of this invention and other paint additives as desired. Useful mineral pigments ordinarily include opacifying pigments such as titanium dioxide, zinc oxide, titanium calcium, as well as tinting pigments such as carbon black, yellow oxides, brown oxides, tan oxides, raw and burnt sienna or umber, chromium oxide green, phthalocyanine green, phthalonitrile blue, ultramarine blue, cadmium pigments, chromium pigments, and the like. Filler pigments such as clay, silica, talc, mica, wollastonite, wood flower, barium sulfate, calcium carbonate and the like can be added.

Historically, prior art paints achieved a balance of properties by making the latex slightly too hard for LTFF to achieve the tack-free character, and then temporarily softening the binder polymer with a coalescing solvent to achieve the desired LTFF. However, by using non-volatile, external softening oligomers in accordance with this invention, the historical relationship between Tg (or MFT) and LTFF in the final paint can be changed such that both film formation and tack free character are simultaneously obtained without the need for a volatile coalescing solvent. The softening oligomer is permanent by design and will not volatilize out of the paint film.

The merits of this invention are further supported by the following illustrative examples.

#### Comparative Examples A and B

A vinyl acetate and butyl acrylate 80/20 copolymer (Ex. A) and a vinyl acetate/butyl acrylate 60/40 copolymer (Ex. B) were produced from the following ingredients.

	Ex. A	Ex. B	
a)	2022 g 7.2 g 4.3 g 5.4 g	2022 g 7.2 g 4.3 g 5.4 g	deionized water MM-80 ammonium acetate A246L
b)	28 g 7.0 g 0.7 g	28 g 7.0 g 0.7 g	vinyl acetate butyl acrylate ammonium persulfate
c)	1360 g 340 g 2.4 g	1034 g 677 g 2.4 g	vinyl acetate butyl acrylate acrylic acid
d)	5.4 g 21 g 135 g 15 g	5.4 g 21 g 135 g 15 g	ammonium persulfate A246L deionized water NaAMPS

Warm (a) to 71°C under nitrogen with good stirring. Add (b) and allow exotherm to die (about 15 minutes). Pump in (c) and (d) in parallel over 5 hours. Hold 1 hour, and cool.

#### Comparative Example

Comparisons of soft copolymer and coalesced hard copolymer (prior art) with the current invention are as follows.

Prior art. Conventionally, the balance of low temperature film formation and absence of tack at ambient temperature is achieved by utilizing a latex composition with an elevated T<sub>g</sub>, to achieve absence of tack, and then temporarily reducing its T<sub>g</sub> with a volatile coalescing solvent such as Texanol, to achieve low temperature film formation. While this works well, it also involves the emission of the coalescing solvent into the atmosphere, which contributes odour and air pollution. A typical copolymer composition comprises by weight 80% vinyl acetate and 20% butyl acrylate, as in Example A above. For this experiment, the latex contained coalescing solvent at the level of 6% to achieve a KMFT of 10°C. A film cast with this coalesced latex was non-tacky at room temperature, but emitted volatile solvent to the atmosphere.

Conversely, if one makes a copolymer with a low enough T<sub>g</sub> to achieve low temperature film formation (60/40 VA/BA), as in Example B above, the polymer forms a film which is excessively tacky at ambient use temperature. While this would involve no VOC emissions to the atmosphere, the coating involves a commercially unacceptable balance of properties. This soft copolymer achieves a KMFT of 10°C on its own. A film cast from this latex is extremely tacky at room temperature, but emits no solvents to the atmosphere.

Present Invention. In the present invention, the use of a non-volatile external plasticizer accomplishes all three goals simultaneously: low temperature film formation, tack-free behavior at ambient temperatures, and no volatile organic emissions to the atmosphere.

#### Example 1

A low molecular weight dipropylene-adipate oligomer polyester was synthesized in accordance with the preferred process at a -OH/-COOH equivalent ratio of 1.25 as follows:

1629.9 grams adipic acid

1870.1 grams dipropylene glycol

1.1 grams butyl stannic acid

The foregoing materials were charged to a flask equipped with a stirrer and heated up to 240°C maximum under nitrogen along with water of reaction removal and held until a final Acid No. of 4 to 8 was obtained based on solids. The resulting polyester had ICI Cone & Plate viscosity 14-18 poise at 30°C, and a number average molecular weight of 800, and a T<sub>g</sub> of -50°C.

The foregoing polyester was used to make an oligomeric pre-emulsion comprising by weight 62.5% polyester, 3.6% Triton X405 surfactant (70% active nonyl phenol ethoxylate), and 33.9% deionized water. This corresponds to 4% surfactant based on the weight of polyester. The pre-emulsion was formed by adding the polyester to the water/surfactant solution with ordinary agitation to form a premix, heating the

premix above 45°C to about 60°C, and then passing the heated premix through a Sonic Triplex Model T02-2A-HP ultrasonic emulsifier equipped with a 0.001 square inch orifice at 1000 psi. The resulting mixture was a stable, water dispersed, pre-emulsion of polyester oligomer having an emulsion particle size less than 0.7 microns. The oligomer pre-emulsion was then blended with 80/20 by weight vinyl acetate butyl acrylate copolymer (Example A above) having a Tg = 10°C at the level of 10% polyester based on the weight of oligomer and latex polymer solids or 800 grams latex 56.5% NV was mixed with 77.3 grams of polyester pre-emulsion. Blending of the oligomer pre-emulsion and latex was at room temperature, mixed thoroughly for about one hour, and then was allowed to set at room temperature for about 24 hours without further mixing. The oligomer modified latex provided an excellent semi-gloss latex paint.

#### Example 2

In a manner similar to Example 1, a low molecular weight polyester prepolymer was prepared at a -OH/-COOH equivalent ratio of 1.186 as follows:

1675.1 grams adipic acid  
1823.4 grams dipropylene glycol  
0.5 grams triphenyl phosphine  
1.1 grams butyl stannic acid

The polyester was synthesized at less than 240°C to obtain a 4-8 Acid No. along with a 32-38 poise viscosity at 30°C, a number average molecular weight of 970, and a Tg of - 50°C. The oligomer pre-mix was micronized through a Sonolator to an emulsion particle size less than 0.7 microns. The oligomer pre-emulsion was mixed with the 80/20 vinyl acetate butyl acrylate copolymer latex in the manner of Example 1.

#### Example 3

White semi-gloss latex paints were prepared from any one of the foregoing emulsion polymers described in Examples 1 or 2 from the following ingredients:

#### PIGMENT GRIND:

Group	Ingredient	Grams
A	Water	151.68
A	Thickener	.50
A	Ammonia (28%)	.01
B	Surfactant	5.00
C	Defoamer	2.00
C	Surfactant	2.00
D	TiO <sub>2</sub> pigment	145.00
D	Clay extender pigment	50.00

Group A ingredients were added to Cowles dispersing equipment and mixed for 5 minutes. Group B and then C ingredients were added with continued mixing under slow agitation. Group D ingredients were added under high speed agitation and grind for 15 minutes or until a Hegman 5.5 was attained. The foregoing is the grind portion of the paint.

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## LETDOWN

Group	Ingredient	Grams
E	Water	33.00
F	Water	33.00
F	Thickener	3.50
F	Ammonia Hydroxide	.01
G	Preservative	1.00
H	Defoamer	5.00
H	Propylene glycol	40.00
H	Surfactant	4.50
H	Rheology Modifier (Ex. 1 or 2)	9.00
H	Surfactant	3.00
I	Latex (Ex. 1 or 2)	393.00
I	Opacifier latex	105.00

Group E ingredients were added in separate vessel, followed by Premix F added to E ingredients with slow speed agitation. Group G ingredients were added at slow speed. Premix H ingredients were then added to vessel. Premix I ingredients were mixed for 30 minutes and then added to vessel. The final composition was mixed for 1 hour. The foregoing is the letdown portion of the paint.

## LATEX PAINT

The letdowns above were added to the pigment grind above under slow speed agitation and allowed to mix for 2 hours. Paint films from the foregoing latex paints were drawn down at 1 mil, air dried for at least 24 hours, and then tested for the following results:

LTFF	Paint Ex. 1	Paint Ex. 2
70°F	pass	pass
50°F	pass	pass
40°F	pass	pass

Dried paint films are considered to pass low temperature film formation (LTFF) if the dried coating has no tacking and is visible under ten-times magnification.

## Example 4

The following data was generated by blending an emulsion of an MPD/ADA modifier (methyl propane diol/adipic acid polyester of MW ca 1200) with the vinyl acetate homopolymer latex. The MPD/ADA oligomer modifier was prepared as in Example 1 by reacting:

- 877 gms of adipic acid
- 630.7 gms of 2-methyl-1,3-propane diol
- 0.2 gms of butylstanoic acid

The emulsion was prepared as in Example 1 with a Ross ME-100L rotor-stator mixer, which produced a sub-micron pre-emulsion in size.

TABLE 1

Effect of Blended Modified on MFT			
PCT Modifier (Ex. 4)	Initial (Ca. 30°C)	After 24 Hours	After 5 Days
20	20	13	18
30	13	9	14
40	10	7	10
0	35		

As can be seen, oligomeric modifier appears to diffuse into the latex, lowering its MFT. The Fox Equation relationship appears to hold quite well for blends of compatible oligomers with latex, and the estimated fraction of the oligomeric modifier which diffused into the latex. Table 2 summarizes these calculations:

TABLE 2

Estimated Extent of Diffusion	
PCT Modifier	Pct Diffused
20	65
30	56
40	50

It was found that the foregoing MPD/ADA oligomeric modifier is effective as a film-forming modifier in accordance with this invention but is not as effective as the adipic acid dipropylene glycol polyester of Examples 1 and 2.

#### Examples 5 - 8

A series of polyester modifiers were prepared as follows:

TABLE 3

	<u>Ex. 5</u>	<u>Ex. 6</u>	<u>Ex. 7</u>	<u>Ex. 8</u>
Neopentyl glycol	416.8	312.6	---	---
Azelaic acid	564.6	376.4	---	---

	Adipic acid	---	---	146.2	
	584.8				
5	Dipropylene glycol	---	---	268.4	---
	Benzoic acid	---	---	183.2	---
10	2-methyl-1,3-				
	propane diol	---	---		---
	180.2				
15	2-ethyl hexanol	---	---		---
	520.8				
20	Butyl stanoic acid	0.2	0.2	0.2	
	0.4				

The polyester oligomers were synthesized as in Example 1.

#### Example 9

A polyester amide was prepared as follows:

13.4 g 2-methyl-1,5-pentane diamine

100.3 g DBE-3 (DuPont, dimethyl adipate)

77.4 g dipropylene glycol

0.1 g butyl stanoic acid

Heat under nitrogen with good agitation to about 220°C. Use a glass bead packed column to distill off methanol, keeping column head temperature at 65°C. Switch to a trap when distillation slows down. Cool after 4 hours at 200°C.

Emulsions of the modifiers were prepared as in Example 1 and blended with a commercial acrylic latex (8°C Tg, DSC, methylmethacrylate-butyl acrylate) and a styrene latex (37°C Tg, DSC, styrene-ethyl-acrylate) as follows:

#### PAINT FORMULA

A) Premix the following components:

	Grams
water	200
cellulosic thickener	1.0
preservative	2.0
defoamer	1.0
polymeric dispersant	6.0
surfactant	4.0

B) Add the following to (A) and disperse 5 minutes at moderate speed:

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	Grams
titanium dioxide	162.7
extender pigment	132.65
crystalline silica	85.65
colloidal silicate	2.00

C) Add the following to (A) and (B) mixture and mix 15 minutes at high speed:

	Grams
water	100
defoamer	2.0

D) Premix the following and then add to the above and mix 15 minutes at low speed:

	Grams
water	60.0
cellulosic thickener	4.5

E) Add the following and mix 15 minutes moderate speed:

	Grams
modified latex	264

F) Add the following components to the above mixture:

	Grams
Water	70
defoamer	3.0
polyurethane associative thickener	10.0

TABLE 4

Acrylic Latex:		
Example	Modifier	40°F LTFF
10	5% Example 5	pass
11	5% Example 6	pass
12	5% Example 7	pass
13	5% Example 8	pass
14	5% Example 9	pass
15	None	fail
Styrene Latex:		
Example	Modifier	70°F LTFF
16	Example 7	pass
17	None	fail



The following examples illustrate the process of this invention where the oligomer is mixed with ethylenic monomer prior to emulsion polymerization. Polyesters with a range of molecular weights and structures can function as effective non-volatile plasticizing and coalescing agents for emulsion addition copolymers, where comonomer is not needed with vinyl acetate polymer and coalescing aid is not required for good film formation. Avoiding the use of coalescing solvents is possible because the higher molecular weight polyesters are dissolved in polyvinyl acetate monomer and then dispersed into water by high shear and/or ultrasound prior to polymerization of the polyvinyl acetate as illustrated in the following examples.

The following examples reflect the process of this invention wherein the oligomer is dispersed into monomer and then micronized into water followed by copolymerization of the monomer.

#### Example 10

An adipate polyester oligomer was prepared as follows:

	Grams
Adipic acid	438.6
Diethylene glycol	382
Butylstanoic acid	0.5

The above raw materials were heated in a 2 liter flask under a nitrogen blanket with mechanical stirring to 170°C while using the head temperature above a column packed with glass beads to regulate the esterification reaction. With a head temperature of 98°C, the reaction temperature increased slowly to 220°C, where the temperature was held for 2 hours and then cooled.

An aqueous suspension of vinyl acetate monomer and the above adipate polyester was prepared from the following materials.

		Grams
a)	deionized water	2000
	MM-80, Mona Chemical <sup>1</sup>	11.2
	(NH <sub>4</sub> ) HCO <sub>3</sub>	2.5
	NaAMPS, Lubrizol Corp.	2.5
	vinyl acetate monomer	625
b)	polyester from above	312
	MT-70, Mona Chemical <sup>2</sup>	5.6
c)	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	5.0
d)	vinyl acetate monomer	625
	MT-70 <sup>3</sup>	5.6

<sup>1</sup>MM-80 = sodium dihexyl sulfosuccinate

<sup>2</sup>NaAMPS = sodium acrylamide methyl propane sulfonate

<sup>3</sup>MT-70 sodium ditridecyl sulfosuccinate

Organic solution (a) was dispersed in aqueous solution (b) with a prop stirrer at about 5000 rpm for 20 seconds and passed through the flow through cell of a Sonics Corp. model VC-600 ultrasonic device at 85% power. The resulting aqueous emulsion was heated with stirring under a nitrogen blanket to 65°C. Component (c) was added and 65°C was held for 1.5 hours. Monomer mixture (d) was added over 3 hours at 72°C, held 1 hour, and then cooled.

#### Example 11

In a manner similar to Example 10, a phthalate polyester oligomer was prepared, mixed with vinyl acetate monomer, micronized into water by high shear, and polymerized. The phthalate polyester was as follows:

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	Grams
phthalic anhydride	593
diethylene glycol	318.3
butyl cellosolve	236.4

The raw materials were heated under nitrogen to 200°C, then slowly raised to 220°C over 2 hours while keeping the head temperature of the packed distillation column at 98°C. Total distillate was 73 g. A suspension of the above phthalate polyester was prepared as follows:

	Grams
a) deionized water	800
MM-80	3.0
NaHCO <sub>3</sub>	2.0
b) vinyl acetate monomer	250
polyester (Ex. 11 above)	80
c) K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	2.0
d) vinyl acetate monomer	250
MT-70	3.0

The procedure for polymerizing the ethylenic monomers was the same as described in Example 10.

Example 12

In a manner similar to Example 11, a polymer was prepared except that the amount of phthalate polyester was increased from 80 grams to 150 grams.

Example 13

In a manner similar to Example 11, a polymer was prepared using the following components using a commercial polyester believed to be a polyether-phthalate-polyester capped with benzoic acid (Hercoflex 900, Hercules Corp.).

	Grams
a) deionized water	2000
MM-80	15
NaHCO <sub>3</sub>	2.5
NaHCO <sub>3</sub>	7.5
NaAMPS	2.5
b) vinyl acetate monomer	625
Hercoflex 900, (Hercules Corp.)	250
c) K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	5.0
d) vinyl acetate monomer	625
MT-70	7.5

The procedure from Example 10 was used to copolymerize the monomers and produce a latex polymer.

Example 14

In a manner similar to Example 10, a polyester triester was prepared from the following reactants:

	Grams
Ektasolve DB, Eastman Chem. (diethylene glycol butyl ether)	365
trimellitic anhydride	145
butylstanoic acid	0.1

The water of reaction distilled off was 29 grams.

A polymer was prepared according to the polymerization process described in Example 12 but from the following components:

		Grams
a)	deionized water	800
	MM-80	3.0
	NaHCO <sub>3</sub>	2.0
b)	vinyl acetate monomer	250
	triester from above	50
	MT-70	1.0
c)	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	2.0
	vinyl acetate monomer	250
	MT-70	3.0

Example 15

Clear unpigmented films were prepared from the polymers prepared in Examples 10-14. Physical properties of latex and air dried clear paint films were as follows:

Suspension Tack	Min. Film Temp. Crack Point	Min. Film Temp. Knife Point
Ex. 10	<3	<3
None		
Ex. 11	12	24
None		
Ex. 12	3	9
None		
Ex. 13	<3	6
None		
Ex. 14	4	15
None		
Control *	10	12
None		

\*Control was an unmodified commercial latex typically used in consumer air-dry paints and comprising 80/20 weight ratio of vinyl acetate polymerized with butyl acrylate.

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## Example 16

White semi-gloss latex paints were prepared from any one of the foregoing emulsion polymers described in Examples 10-14 from the following ingredients: Pigment Grind:

Group	Ingredient	Grams
A	Water	151.68
A	Thickener	.50
A	Ammonia (28%)	.01
B	Surfactant	5.00
C	Defoamer	2.00
C	Surfactant	2.00
D	TiO <sub>2</sub> pigment	145.00
D	Clay extender pigment	50.00

Group A ingredients were added to Cowles dispersing equipment and mixed for 5 minutes. Group B and then C ingredients were added with continued mixing under slow agitation. Group D ingredients were added under high speed agitation and grind for 15 minutes or until a Hegman 5.5 was attained. The foregoing is the grind portion of the paint.

Letdown	Ingredient	Grams
E	Water	33.00
F	Water	33.00
F	Thickener	3.50
F	Ammonia Hydroxide	.01
G	Preservative	1.00
H	Defoamer	5.00
H	Propylene glycol	40.00
H	Surfactant	4.50
H	Rheology Modifier	9.00
H	Surfactant	3.00
I	Latex	393.00
I	Opacifier latex	105.00

Group E ingredients were added in separate vessel, followed by Premix F added to E ingredients with slow speed agitation. Group G ingredients were added at slow speed. Premix H ingredients were then added to vessel. Premix I ingredients were mixed for 30 minutes and then added to vessel. The final composition was mixed for 1 hour. The foregoing is the letdown portion of the paint.

## Latex Paint

The letdown above was added to the pigment grind above under slow speed agitation and allowed to mix for 2 hours.

Example 17

Benzoic acid capped polyester oligomer modifier.

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10

Ingredient	Grams
adipic acid	731
diethylene glycol	637
butylstanoic acid	0.5
benzoic acid	244

Heat the above components gradually with adequate stirring under a nitrogen atmosphere to 220°C. (Water will begin to distill at about 170°C, and about 3 hours will be required to move the batch from 170°C to 220°C). Using a packed column, maintain the head temperature at 99°C throughout this portion of the synthesis. When the head temperature drops below 80°C, remove the column and replace with a Dean-Stark trap. Fill the trap with xylene, and then add just enough additional xylene to give a constant reflux. Allow xylene reflux to azeotrope water out of the batch, and reduce acid number to about 10 mg KOH/g resin. Remove xylene under a vacuum (25 inches Hg). Cool.

20

Example 18

Benzoic acid capped polyester urethane oligomer modifier

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As in Example 17, but use only 122 g benzoic acid, then cool batch to 60°C at the end of the synthesis, and add 111 g isophorone diisocyanate. Allow the exotherm to carry the temperature (with gentle heating) to 90°C, and hold for 2 hours. Cool.

30

Example 19

Polyester urethane oligomeric external modifier

35

Ingredient	Grams
adipic acid	731
diethylene glycol	636
butylstanoic acid	0.5

40

Synthesize a polyester from the above ingredients in the same manner as in Example 17, and then add 111 g isophorone diisocyanate to form a polyester urethane as in Example 18.

Example 20

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Polyester urethane external modifier

50

Ingredient	Grams
adipic acid	366
dipropylene glycol	403
butylstanoic acid	0.2

55

Form a polyester from the above ingredients as in Example 17, and then add 56 g isophorone diisocyanate to form a urethane as in Example 18.

Example 21

Polyester urethane urea oligomeric external modifier

5

Ingredient	Grams
adipic acid	731
dipropylene glycol	805
butylstanoic acid	0.5

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15

Synthesize a polyester from the above as in Example 17, and place 300 g of the product in a separate flask at 20°C. Add 29 g isophorone diisocyanate and 30 g Jeffamine ED-2001 polyethylene oxide diamine, 2000 mol. wt. no. ave. - Texaco. The Jeffamine is predissolved in 30 g vinyl acetate to enhance miscibility. Slowly warm to 40°C to allow amine reaction with isocyanate, hold 1 hour, and then heat to 90°C. Hold 2 hours, and then cool.

Example 22

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Polyester amide external oligomer modifier

25

Ingredient	Grams
DBE-5 (dimethyl ester of glutaric acid, DuPont)	481
dipropylene glycol	268
Dytek A (2-methylpentane diamine)	58
butylstanoic acid	0.2

30

Warm with good agitation under nitrogen to about 190°C and distill off methanol with a good packed column. Keep column head temperature at 64°C, and gradually warm batch to 210°C. Cool after 160 g of methanol is removed.

35 Example 23

Polyester amide external oligomer modifier

40

Ingredient	Grams
DBE-5	481
dipropylene glycol	268
Jeffamine D-230 (polypropylene oxide diamine)	115
butylstanoic acid	0.5

45

Synthesized by same procedure as in Example 22.

50

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Example 24

Polyester external oligomer modifier

Ingredient	Grams
dipropylene glycol	4717
adipic acid	4283
triphenyl phosphine	1.2
butylstanoic acid	3.0

Synthesize as in Example 17, but do not use xylene. When column head temperature drops to 80°C acid number is about 20 mg KOH/g resin. Pull a vacuum of about 10 inches of Hg, and then gradually increase vacuum to pull off remaining water. Final acid number is 3 mg KOH/g resin.

Example 25

Latexes were prepared with the following generalized formula and synthesized as described below.

a)	2122 g 8.5 g 5.4 g 8.1 g 10.5 g	deionized water MA-80 (dihexyl sulfosuccinate, Mona Chem.) ammonium acetate Na AMPS, 48% (Lubrizol Chemical) A246L (Na olefin sulfonate, Rhone Poulenc)
b)	7.4 g 10 ml	Na formaldehyde sulfoxylate FeSO <sub>4</sub> aqueous solution, 1000 ppm
c)	869 g 370 g 3.1 g	vinyl acetate modifier as above from Examples 8 to 16 acrylic acid
d)	6.3 g 14 g 159 g	ammonium persulfate A246L deionized water
e)	874 g 3.1 g	vinyl acetate acrylic acid
f)	2.0 g 27 g	ammonium persulfate deionized water

Weigh and mix thoroughly groups (a) and (c). Combine groups (a) and (c), stir with a spatula to disperse, and then emulsify for 5 minutes at 10,000 rpm in a Ross ME 100L emulsifier. Add (b) ingredients to the emulsion, and warm in a 5 liter Morton flask to 50°C with good agitation under nitrogen. Pump in 40 ml of (d) over 2.5 hours, adjusting pumping rate to give a reaction temperature of about 55°C. Pump in the rest of (d) and all of (e) over 3 hours. Pump in (f) over 1 hour. Cool.



Examples 26-33 Latexes approximately equivalent were prepared as in Example 25 and mixed with modifiers identified in the following Table.

TABLE

Ex. Tack	Modifier	DSC Tg	Knife Point MFFT	Dry Film
26	Ex. 17	0	8.2	None
27	Ex. 18	11	8.8	None
28	Ex. 19	11	12.5	None
29	Ex. 20	10	13.7	None
30	Ex. 21	13	19.5	None
31	Ex. 22	6	7.6	None
32	Ex. 23	-5	10.0	Tacky
33	Ex. 24	—	16.5	None

\*DSC Tg's in degrees C (single, distinct transitions are noted). MFFT = minimum film formation temperature in degree C (knife point). Tack and MFFT were measured for dry latex films (only DSC Tg was measured for modifiers).

The film from Example 32 is tacky at room temperature, while the other latexes form good, tack free films. Generally, Tg's in the 5-10°C range are preferred. MFFT's of 20°C or less are preferred, indicating that good ambient and low temperature film formation will occur. Example 32 was marginally tacky due to low Tg of the film.

#### Examples 34-38

Polymeric binders containing chlorinated aliphatic modifier were prepared as follows:-

	<u>Ex.34</u>	<u>Ex.35</u>	<u>Ex.36</u>	<u>Ex.37</u>	<u>Ex.38</u>
a) Deionized water	800	800	800	800	2000
5 MM-80, Mona Chem <sup>1</sup>	6.0	6.0	6.0	6.0	15
NaHCO <sub>3</sub>	1.0	1.0	1.0	1.0	2.5
10 NaAMPS Lubrizol <sup>2</sup>	1.0	1.0	1.0	1.0	2.5
b) Vinyl acetate					
monomer	250	250	250	250	625
16 DA-8527, Dover <sup>3</sup>	-	100	-	-	250
DA-8506, Dover <sup>4</sup>	100	-	-	-	-
20 Paroil 10 Dover <sup>5</sup>	-	-	100	-	-
Paroil 170-LV Dover <sup>6</sup>	-	-	-	100	-
MT-70, Mona Chem. <sup>7</sup>	3.0	3.0	3.0	3.0	7.5
25 c) K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	2.0	2.0	2.0	2.0	5.0
d) vinyl acetate					
30 monomer	250	250	250	250	625
MT-70	3.0	3.0	3.0	3.0	7.5

35 <sup>1</sup>MM-80 is sodium dihexyl sulfosuccinate.

<sup>2</sup>NaAMPS is sodium acrylamide methyl propane sulfonate.

40 <sup>3</sup>DA-8527 is a chlorinated fatty acid with 29% chlorine.

<sup>4</sup>DA-8506 is a chlorinated fatty acid ester, with 35% chlorine.

45 <sup>5</sup>Paroil 10 is a chlorinated parafin with 41% chlorine.

<sup>6</sup>Paroil 170-LV is a chlorinated parafin with 67% chlorine.

50 <sup>7</sup>MT-70 is sodium tridecyl sulfosuccinate

Solution (b) was prepared and dispersed into solution (a) at 5,000 rpm with a lab 1.5 inch prop stirrer. The resulting organic mixture was passed through Sonics Corp. VA-600 ultrasonics unit equipped with a flow  
55 through cell, one pass at 85% power to produce an organic phase dispersed in water. Component (c) was added, heated to 65°C and held 1.5 hours. Monomers (d) were fed in over three hours at 72°C, held 1 hour, and then the reaction mixture was cooled to room temperature.

Clear films were air dried at room temperature for 24 hours. Dried film properties were as set forth in following Table 1:

Table 1

Example	MFT Crack	MFT Knife	Water Rubs	Water Whitening	Tack
1	9C	18C	200 +	Moderate	None
2	<2C	10C	200 +	Moderate	v.sl.
3	<3C	9C	200 +	Moderate	None
4	12C	26C	200 +	Moderate	None
5	3C	14C	200 +	Mild	None

### Claims

1. An aqueous air-dry coating composition including an emulsion polymerised polymeric binder having a Tg below 20°C which binder contains an addition copolymer of aqueous polymerised ethylenic monomers wherein the binder also contains 3 to 70% of an oligomer modifier selected from a polyurethane, a polyester, a chlorinated hydrocarbon and/or a chlorinated fatty acid or fatty acid ester, the oligomer modifier having a molecular weight between 200 and 20,000 and a Tg below -20°C and wherein the oligomer modifier is present in the aqueous composition as a micro-emulsion of droplets having a droplet size of less than 10 microns.
2. An aqueous air-dry coating composition as claimed in Claim 1 containing an emulsion polymerized polymeric binder free of organic coalescing solvent, the polymeric binder comprising:  
an addition copolymer of aqueous polymerized ethylenic monomers containing an oligomer modifier having a molecular weight between about 200 and 20,000 and a Tg below about -20°C, the oligomer selected from a polyurethane, a polyester, a chlorinated hydrocarbon and/or a chlorinated fatty acid or fatty acid ester, where the oligomer is dispersed into water by high shear mixing to provide a micro-emulsion having a droplet size less than 10 microns, where the polymeric binder comprises by weight between 3% and 70% of said oligomer with the balance being said addition copolymer, where the Tg of the polymeric binder is less than 20°C.
3. A coating composition as claimed in Claim 1 or Claim 2 containing the low molecular weight oligomeric modifier in an aqueous micro-emulsion having an organic phase emulsion droplet size less than 10 microns and produced by high shear mixing at temperatures between 20°C and 100°C of an aqueous mixture of the oligomer and water where the mixture contains between 40% and 70% oligomer, and the oligomer has a number average molecular weight between about 300 and 5,000 and a Tg less than -20°C.
4. A coating composition as claimed in any one of the preceding Claims containing between 3% and 50% by weight of the oligomer modifier, where said polymeric binder is produced by mixing the oligomer in the ethylenic monomer to provide an organic solution of oligomer and ethylenic monomer, where said organic solution is dispersed into and polymerized in water to produce an oligomer modified addition copolymer emulsion polymer where the oligomer is soluble in the polymerized monomer.
5. A coating composition as claimed in Claim 3 where the oligomeric modifier has a molecular weight between 500 and 2,000.
6. A coating composition as claimed in Claim 3 or Claim 4 where the oligomeric modifier has a molecular weight between 500 and 1,000.
7. A coating composition as claimed in any one of Claims 3 to 6 where the aqueous mixture comprises by weight between about 55% and 65% oligomer modifier forming the micro-emulsion.
8. A coating composition as claimed in any one of the preceding Claims where the micro-emulsion was produced by high shear mixing of the aqueous mixture of oligomer at temperatures between 45°C and

60°C.

9. A coating composition as claimed in any one of Claims 1 to 8 wherein the micro-emulsion droplet size is on average between 0.1 and 1 micron.
10. A coating composition as claimed in any one of Claims 1 to 9 wherein the average emulsion droplet size is below 0.7 microns.
11. A coating composition according to any one of Claims 1 to 10 where the oligomer has a Tg less than about -40°C.
12. A coating composition according to any one of Claims 1 to 11 where the oligomer has a Tg less than about -50°C.
13. A coating composition according to any one of Claims 3 to 12 where the oligomer has a molecular weight between about 300 and 10,000.
14. A coating composition according to any one of Claims 3 to 13 where the oligomer has a molecular weight between about 500 and 5,000.
15. A coating composition according to any one of Claims 3 to 14 where the polymeric binder is produced by micronizing the aqueous dispersion with high shear to a micronized aqueous dispersion having organic phase particle size droplets less than 5 microns.
16. A coating composition according to any one of the preceding claims where the oligomer is a polyurethane.
17. A coating composition according to Claim 16 where the polyurethane oligomer comprises a polyester-urethane copolymer.
18. A coating composition according to Claim 16 where the polyurethane oligomer comprises a polyurethane-urea copolymer.
19. A coating composition according to any of the Claims 1 to 15 where the oligomer is a polyester polymer.
20. A coating composition of Claim 19 where the polyester oligomer comprises a polyester-amide copolymer.
21. A coating composition according to any one of Claims 1 to 15 where the oligomer is a chlorinated hydrocarbon, a chlorinated fatty acid or a chlorinated fatty acid ester.
22. A coating composition according to any one of the preceding Claims where the addition polymer comprises emulsion copolymerized vinyl acetate monomer.
23. A coating composition according to any one of the preceding Claims where the addition polymer comprises emulsion copolymerized acrylic monomer.
24. A coating composition according to Claim 23 where the addition polymer comprises emulsion copolymerized acrylic monomer and styrene.
25. A coating composition according to Claim 4 where the polymeric binder contains between 10% and 25% of said oligomer.
26. A process for producing an aqueous ambient dry coating composition containing a polymeric binder free of organic coalescing solvent, the process steps for producing the polymeric binder comprising:  
producing a micronized, aqueous pre-emulsion of oligomer modifier selected from a polyurethane, a polyester, a chlorinated hydrocarbon and/or a chlorinated fatty acid or fatty acid ester, the pre-

emulsion having an organic phase droplet size less than 10 microns by high shear mixing at temperatures between 20°C and 100°C of an aqueous mixture of the oligomer containing by weight between 40% and 70% oligomer, where the oligomer has a Tg less than -20°C and number average molecular weight between about 300 and 5,000;

5 mixing the pre-emulsion with an emulsion copolymerized addition polymer comprising ethylenically unsaturated monomers to produce a polymeric binder containing by weight between about 3% and 30% oligomer, where the polymeric binder has a Tg less than 20°C.

10 27. A process according to Claim 26 where micronizing produces a micro-emulsion having an organic phase particle size droplet less than 1 micron.

28. A process according to Claim 26 or Claim 27 where the micronizing produces organic phase particle size droplets less than 0.7 microns.

15 29. A process according to any one of Claims 26 to 28 where the micro-emulsion is formed at temperatures between about 45°C and 60°C.

30. A process according to any one of Claims 26 to 29 where the oligomer has a molecular weight between 500 and 2,000.

20 31. A process for producing an aqueous ambient dry paint coating containing a polymeric binder free of organic coalescing solvent, the process steps for producing the polymeric binder comprising:

25 providing an organic solution comprising vinyl acetate monomer and oligomer having a number average molecular weight between 200 and 20,000 and selected from a polyurethane, a polyester, a chlorinated hydrocarbon and/or a chlorinated fatty acid or fatty acid ester, the oligomer having a Tg below about -20°C, where the organic solution contains at least 3% by weight of said oligomer;

dispersing the organic solution into water to produce an aqueous dispersion;

micronizing the aqueous dispersion under high shear to produce a micro-dispersion having organic phase particle size droplets less than 5 microns; and

30 polymerizing the vinyl acetate monomer to produce a polymeric binder having a Tg less than 20°C comprising an emulsion vinyl acetate polymer containing said oligomer.

32. A process according to Claim 30 where micronizing produces organic phase particle size droplets less than 1 micron.

35 33. A process according to Claim 31 or Claim 32 where the micronizing produces organic phase particle size droplets less than 0.7 microns.

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71 Applicant: **THE GLIDDEN COMPANY**  
925 Euclid Avenue  
Cleveland Ohio 44115 (US)

72 Inventor: **Craun, Gary Pierce**  
409 Crescent Drive  
Berea, Ohio 44017 (US)  
Inventor: **Rosekelly, George Stephne**  
15209 Athens Avenue  
Lakewood, Ohio 44107 (US)  
Inventor: **Floyd, Frederick Louis**  
1400 East-West Highway,  
Apartment 523  
Silver Springs, Maryland 20910 (US)

74 Representative: **Cooper, Alan Victor et al**  
Patents and Trade Marks Section  
Legal Affairs Department  
ICI Paints  
Wexham Road  
Slough SL2 5DS (GB)

54 **Latex paints with microemulsion modifier and process for their preparation.**

57 An aqueous ambient dry paint coating based on an addition copolymer matrix polymer containing an oligomer selected from a polyurethane or a polyester having a T<sub>g</sub> below -20°C and a number average molecular weight between 200 and 20,000, where the coating is free of organic coalescing solvents. The matrix polymer comprises emulsion copolymerized ethylenic monomers. In a preferred process, the oligomer is produced by forming an aqueous micro-preemulsion of oligomer in water by high shear mixing of oligomer and water containing 40% to 70% by weight oligomer and at temperatures between about 20°C and 100°C to provide an aqueous pre-emulsion having an organic phase droplet size less than 10 microns. The polymeric binder can be produced also by mixing the oligomer with the ethylenic monomers to form an organic mixture of monomer and oligomer, providing an

aqueous micro dispersion of the organic mixture phase droplet size less than 5 microns, and copolymerizing the monomer to produce a vinyl acetate polymer containing oligomer. The polymeric binder system is free of coalescing organic solvent.

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# EUROPEAN SEARCH REPORT

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
X	EP-A-0 401 565 (PPG IND INC) * claims 1,4-6,9; examples i-iii * ----	1	C09D5/02 C09D157/00 C08J3/02 C08F2/22
X	EL-NOKALY 'polymer association structures' , ACS , NEW ORLEANS US , XPBOOK: EL-N * chapter 7, "Preparation of microlatex with functionalized polyesters as surfactants", F. Cuirassier et al. * page 100 - page 115 * -----	1	
			TECHNICAL FIELDS SEARCHED (Int.Cl.5)
			C09D C08F
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 2 May 1994	Examiner Dieter Schüler
<b>CATEGORY OF CITED DOCUMENTS</b> X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document			





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### CLAIMS INCURRING FEES

The present European patent application comprised at the time of filing more than ten claims.

- ☐ All claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for all claims.
- ☐ Only part of the claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims and for those claims for which claims fees have been paid, namely claims:
- ☐ No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims.

### LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirement of unity of invention and relates to several inventions or groups of inventions, namely:

see sheet -B-

- ☐ All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.
- ☐ Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid, namely claims:
- ☒ None of the further search fees has been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims.

namely claims: mentioned in item 1.



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EP 94 10 1602 -B-

**LACK OF UNITY OF INVENTION**

The Search Division considers that the present European patent application does not comply with the requirement of unity of invention and relates to several inventions or groups of inventions, namely:

1. Claims 1-31 (partially): Latex-binders with oligomeric polyurethane or polyester
2. Claims 1-31 (partially): Latex binders with chlorinated organic compounds

